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FOR: LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS  
PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY  
CELL EMPLOYING IT, AND LITHIUM SECONDARY CELL

DECLARATION

COMMISSIONER FOR PATENTS

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SIR:

Now comes MASAYUKI KUWANO who deposes and says:

That my name is MASAYUKI KUWANO ;

That my address is 5-24-310, 3-chome, Nakacho, Musashino-shi,  
Tokyo, Japan;

That I know well both the English and Japanese languages;

That the attached English language translation is true and  
correct translation of Japanese Patent Application No. JP11-287785 filed on  
October 8, 1999 to the best of my knowledge and belief;

I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

FURTHER DEPONENT SAITH NOT.

September 21, 2006  
Date

Masayuki Kuwano  
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Applicant:

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【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

PROCESS FOR PRODUCING LITHIUM-COBALT COMPOSITE OXIDE

【SCOPE OF THE CLAIM(S)】

5       【Claim 1】

A process for producing a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula  $\text{LiCoO}_2$ , and which has a half-width of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , of from  $0.070$  to  $0.110^\circ$ , as measured by the X-ray diffraction using  $\text{CuK}_\alpha$  as a ray source; which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from  $1$  to  $20 \mu\text{m}$  and a specific surface area of from  $2$  to  $200 \text{ m}^2/\text{g}$ , a lithium carbonate powder having an average particle size of from  $1$  to  $50 \mu\text{m}$  and a specific surface area of from  $0.1$  to  $10 \text{ m}^2/\text{g}$ , and firing the mixture at a temperature of from  $850$  to  $950^\circ\text{C}$  in an oxygen-containing atmosphere for from  $4$  to  $30$  hours.

      【Claim 2】

20       The process for producing a hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, wherein the half-width of the diffraction peak for (110) face is from  $0.080$  to  $0.100^\circ$ .

      【Claim 3】

25       The process for producing a hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to

Claim 1 or 2, wherein the packing press density of the hexagonal lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm<sup>3</sup>.

【DETAILED DESCRIPTION OF THE INVENTION】

5       【Technical Field to which the Invention Belongs】

The present invention relates to an improved process for producing a lithium-cobalt composite oxide for a lithium secondary cell.

      【Prior Art】

10       In recent years, along with the progress in portable or codeless equipments, a demand is mounting for a non-aqueous electrolyte secondary cell which is small in size and light in weight and has a high energy density. As an active material for a non-aqueous electrolyte secondary  
15 cell, a composite oxide of lithium and a transition metal, such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> or LiMnO<sub>2</sub>, has been known.

      Especially, a lithium secondary cell employing a lithium-cobalt composite oxide (LiCoO<sub>2</sub>) as a positive  
20 electrode active material and employing a lithium alloy or a carbon such as graphite or carbon fiber as a negative electrode, provides a high voltage at a level of 4 V and is widely used as a cell having a high energy density.

25       However, there have been a problem of deterioration of the cycle characteristics such that the cell discharge capacity gradually decreases as a charge/discharge cycle

is repeated, or a problem that the safety is insufficient. Further, higher densification is required with respect to the volume capacity density.

In order to improve such cell properties, JP-A-10-  
5 1316 proposes a production method which comprises dispersing in an aqueous lithium hydroxide solution e.g. cobalt hydroxide or cobalt oxyhydroxide wherein the valence of cobalt is trivalent, followed by heat treatment, for the purpose of improving the cycle  
10 characteristics, etc.

Further, JP-A-10-279315 proposes to obtain an active material having a high capacity and good cycle characteristics by firing e.g. dicobalt trioxide or cobalt oxyhydroxide wherein the valence of cobalt is  
15 trivalent, with e.g. lithium oxide at a temperature of from 250 to 1,000°C.

Further, JP-A-10-312805 proposes to improve the cycle characteristics of a secondary cell by using as a positive electrode active material  $\text{LiCoO}_2$  of a hexagonal  
20 system having a crystallite diameter of from 45 to 100 nm in a (110) direction of the crystallite, wherein the length of c axis of lattice constant is at most 14.051 Å.

**【Problems that the Invention is to Solve】**

However, with respect to a lithium secondary cell  
25 using  $\text{LiCoO}_2$  as a positive electrode active material, no product has been known which fully satisfies all of requirements for cycle characteristics, the initial



weight capacity density, the volumetric capacity density and safety, and for a production method for efficient mass production.

**【Means of Solving the Problems】**

5       The present inventors have made extensive studies and, as a result, found that when a positive electrode active material having a specific crystalline structure is used, a large capacity density is obtained, and the cycle characteristics, safety and mass production  
10   property of a secondary cell can remarkably be improved.

      According to the present invention, a positive electrode active material having the above specific crystalline structure can be obtained by dry blending a cobalt oxyhydroxide powder having an average particle  
15   size of from 1 to 20  $\mu\text{m}$  and a specific surface area of from 2 to 200  $\text{m}^2/\text{g}$ , a lithium carbonate powder having an average particle size of from 1 to 50  $\mu\text{m}$  and a specific surface area of from 0.1 to 10  $\text{m}^2/\text{g}$ , followed by firing from 850 to 950°C in an oxygen-containing atmosphere for  
20   from 4 to 30 hours. This active material is represented by the formula  $\text{LiCoO}_2$ , which has a half-width of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , of from 0.070 to 0.110°, as measured by the X-ray diffraction using  $\text{CuK}_\alpha$  as a ray source.

25       The half-width of the diffraction peak for (110) face at  $2\theta = 66.5 \pm 1^\circ$ , as measured by the X-ray diffraction using  $\text{CuK}_\alpha$  as a ray source, of the above lithium-cobalt

composite oxide, reflects the crystallite diameter in a certain specific direction of the lithium-cobalt composite oxide, and a relation has been found such that the larger the half width of the peak, the smaller the crystallite diameter. In the present invention, the half-width of the peak means the width of the peak at 1/2 of the height of the peak.

If the half-width of the diffraction peak for (110) face is less than  $0.070^\circ$ , the charge/discharge cycle durability, initial electric capacity, average discharge voltage or safety of a secondary cell employing it as a positive electrode active material, tends to deteriorate, such being undesirable. If the half-width of the diffraction peak for (110) face exceeds  $0.110^\circ$ , the initial electric capacity and safety of the secondary cell tend to be low, such being undesirable. The particularly preferred range of the half-width of the diffraction peak for (110) face is from  $0.080^\circ$  to  $0.100^\circ$ .

In the present invention, the average particle size means a weight average particle diameter. In the present invention, the average particle size is a particle size at a point where the cumulative curve of mass becomes 50% in the cumulative curve for the total mass of 100% prepared by obtaining the particle size distribution based on mass. This may be referred to also as a mass base cumulative 50% diameter (for example, Chemical Engineering Handbook "Fifth Edition" (compiled by

Chemical Engineering Association) p 220-221. The measurement of the particle size is carried out by thoroughly dispersing in a medium such as water by means of e.g. ultrasonic treatment and measuring the particle size distribution (for example, by using Microtruck HRAX-100, manufactured by Nikkiso co., Ltd.).

For the process of the present invention, cobalt oxyhydroxide of specific properties is used as a cobalt material. If the average particle size of the cobalt oxyhydroxide is less than 1  $\mu\text{m}$ , the safety of the cell tends to decrease, or the packing density of the positive electrode layer tends to decrease, whereby the electrical capacity per volume tends to decrease, such being undesirable. Further, if the weight average particle size of the cobalt oxyhydroxide exceeds 20  $\mu\text{m}$ , the initial capacity tends to decrease and the discharge characteristics of the secondary cell at a large current tend to decrease, such being undesirable. A particularly preferred weight average particle size of the cobalt oxyhydroxide is from 4 to 15  $\mu\text{m}$ .

The above-described cobalt oxyhydroxide may sometimes be produced in a hydrous state. In such a case, the specific surface area can hardly be measured. Accordingly, in the present invention, the specific surface area of cobalt oxyhydroxide means the specific surface area with respect to a powder obtained by drying the hydrous cobalt oxyhydroxide at 120°C for 16 hours for

dehydration.

In the present invention, when hydrous cobalt oxyhydroxide is to be used, it is preferred to use a powder after drying it. For example, it is preferred to  
5 employ it after drying at 120°C for 16 hours.

In the present invention, if the specific surface area of the cobalt oxyhydroxide is less than 2 m<sup>2</sup>/g, the discharge capacity at a large current tends to decrease, such being undesirable. Further, if the specific surface  
10 area of the cobalt oxyhydroxide exceeds 200 m<sup>2</sup>/g, the packing density of the positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A particularly preferred specific surface area of the cobalt  
15 oxyhydroxide is from 20 to 100 m<sup>2</sup>/g.

For the process of the present invention, it is preferred to use lithium carbonate having a specific nature, as a lithium material. If the weight average particle size of the lithium carbonate is less than 1 μm,  
20 the bulk density of the powder tends to decrease, and the productivity in mass production tends to decrease, such being undesirable. Further, if the weight average particle size of the lithium carbonate exceeds 100 μm, the initial electric capacity tends to decrease, such  
25 being undesirable. A particularly preferred weight average particle size of the lithium carbonate is from 5 to 30 μm.

If the specific surface area of the lithium carbonate is less than  $0.1 \text{ m}^2/\text{g}$ , the initial discharge capacity per unit weight tends to decrease, such being undesirable. Further, if the specific surface area of the lithium carbonate exceeds  $10 \text{ m}^2/\text{g}$ , the packing density of the positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A particularly preferred specific surface area of the lithium carbonate is from  $0.3$  to  $3 \text{ m}^2/\text{g}$ .

In the present invention, the cobalt oxyhydroxide powder and the lithium carbonate powder are dry blended, and then fired from  $850$  to  $950^\circ\text{C}$  for from  $4$  to  $30$  hours in an oxygen-containing atmosphere. If the firing temperature is lower than  $850^\circ\text{C}$ , the safety tends to deteriorate and the charge/discharge cycle durability tends to be low, such being undesirable. On the other hand, if the firing temperature exceeds  $950^\circ\text{C}$ , the initial electric capacity tends to decrease, such being undesirable. Particularly preferred is from  $880$  to  $920^\circ\text{C}$ .

If the firing time is less than  $4$  hours, the firing state tends to be non-uniform during mass production, whereby fluctuation is likely to result in the properties, such being undesirable. If it exceeds  $30$  hours, the productivity tends to decrease, such being undesirable. It is particularly preferred to employ a

firing time of from 8 to 20 hours.

The firing of the above mixture is carried out preferably in an oxygen-containing atmosphere. The oxygen concentration in the stream is preferably from 10 to 100 volume%, particularly preferably from 19 to 50 volume%. If the oxygen concentration is low, the cell performance tends to deteriorate, such being undesirable. A secondary cell employing an active material obtained by the process of the present invention and having the specific value of the half-width of the diffraction peak for (110) face, has a higher safety than ever, and is excellent in the charge/discharge cycle durability, while maintaining the initial electric capacity.

Among the lithium-cobalt composite oxides of the present invention, one wherein the packing press density of the lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm<sup>3</sup>, is preferred, since the capacity density per unit volume of the electrode layer of the positive electrode, can be made high. In the present invention, the packing press density means an apparent density of a press-molded product when the lithium-cobalt composite oxide powder is pressed under a load of 1 t/cm<sup>2</sup>.

If the packing press density is less than 2.90 g/cm<sup>3</sup>, the density of the electrode layer of the positive electrode at the time of coating and pressing tends to be low, whereby the capacity per volume tends to be low, such being undesirable. If the packing press density

exceeds  $3.35 \text{ g/cm}^3$ , the capacity development at a high current density of the cell tends to deteriorate, such being undesirable. The packing press density of the lithium-cobalt composite oxide is particularly preferably  
5 from  $3.05$  to  $3.25 \text{ g/cm}^3$ .

A positive electrode composite material is obtained by mixing a binder with the electrically conductive material, a carbon type conductive material such as acetylene black, graphite or ketjenblack, is, for  
10 example, preferably employed. As the binder, polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose or an acrylic resin may, for example, be employed.

In the present invention, a kneaded product or a  
15 slurry comprising the powder of the composite oxide of the present invention, an electrically conductive material, a binder and a solvent or dispersant for the binder, is coated on a positive electrode current collector made of e.g. an aluminum foil or a stainless  
20 steel foil to have it supported on the current collector to obtain a positive electrode plate. As the separator, a porous polyethylene film or a porous polypropylene film may, for example, be employed.

In the lithium secondary cell using the composite  
25 oxide of the present invention as the positive electrode active material, as the solvent for the electrolyte solution, a carbonic ester is preferred. The carbonic

ester may be cyclic or chain. The cyclic carbonic ester may, for example, be propylene carbonate or ethylene carbonate (EC). The chain carbonic ester may, for example, be dimethyl carbonate, diethyl carbonate (DEC),  
5 ethylmethyl carbonate, methylpropyl carbonate or methylisopropyl carbonate.

In the present invention, the above carbonic esters may be used alone or in combination as a mixture of two or more of them. Further, such an ester may be mixed  
10 with other solvent. Further, depending upon the material for the negative electrode active material, there may be a case where the charge/discharge characteristics, cycle durability or charge/discharge efficiency can be improved by a combined use of a chain carbonic ester and a cyclic  
15 carbonic ester.

Further, to such a solvent, a vinylidene fluoride/hexafluoropropylene copolymer (for example, Keiner, tradename, manufactured by Atochem Company) and vinylidene fluoride/perfluoropropyl vinyl ether copolymer  
20 disclosed in JP-A-10-294131, may be added, and the following solute may be added to obtain a gel polymer electrolyte.

As the solute, it is preferred to use at least one member of lithium salts containing e.g.  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  
25  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{CF}_3\text{CO}_2^-$  or  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  as an anion. The elute (for example, the above lithium salt) in the above electrolyte solution or polymer electrolyte,



is preferably contained at a concentration of from 0.2 to 2.0 mol/l. If the concentration departs from this range, the ion conductivity tends to decrease, and the electrical conductivity of the electrolyte tends to decrease. The concentration is more preferably adjusted to be from 0.5 to 1.5 mol/l.

In the secondary cell employing a positive electrode active material of the present invention, as the negative electrode active material, a material capable of absorbing and desorbing lithium ions, is employed. The material for such a negative electrode active material is not particularly limited so long as it has such a property, but, it may, for example, be a lithium metal, a lithium alloy, a carbon material, an oxide composed mainly of a metal of Group 14 or 15 of the Periodic Table, a carbon compound, a silicon carbide compound, a silicon oxide compound, titanium sulfide or a boron carbide compound.

As the carbon material, one obtained by thermally decomposing an organic material by various thermal decomposition conditions, or artificial graphite, natural graphite, soil graphite, expanded graphite or scaly graphite, may, for example, be used. Further, as the oxide, a compound composed mainly of tin oxide, may be used. As the negative electrode current collector, a copper foil or a nickel foil may, for example, be used.

The positive electrode and the negative electrode of

the secondary cell using the positive electrode active material in the present invention are obtained preferably by kneading the active material with an organic solvent to obtain a slurry, and coating the slurry on a metal foil current collector, followed by drying and pressing. There is no particular restriction as to the shape of the lithium cell. A sheet shape (so-called film shape), folded-shape, wounded bottomed cylindrical shape or a button shape, may suitably be selected depending upon the particular application.

【Examples】

Now, the present invention will be described in further detail with reference to Examples, but it should be understood that the present invention is by no means restricted to such Examples.

EXAMPLE 1

A cobalt oxyhydroxide powder having a weight average particle size of 15  $\mu\text{m}$  and a specific surface area of 60  $\text{m}^2/\text{g}$ , and a lithium carbonate powder having a weight average particle size of 15  $\mu\text{m}$  and a specific surface area of 1.2  $\text{m}^2/\text{g}$ , were mixed. The mixing ratio was such that the composition would be  $\text{LiCoO}_2$  after firing. These two types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing, the X-

ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}_\alpha$  ray, the half-width of the diffraction peak for (110) face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.091^\circ$ . The lithium cobalt composite oxide powder was pressed under  $1 \text{ t/cm}^2$ . The packing press density was determined from the volume and the weight, and found to be  $3.18 \text{ g/cm}^3$ .

The  $\text{LiCoO}_2$  powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of  $150 \text{ }\mu\text{m}$ .

And, two stainless steel simple closed cells were assembled in an argon glove box, by using an aluminum foil having a thickness of  $20 \text{ }\mu\text{m}$  as a positive electrode current collector, using a porous polypropylene film having a thickness of  $25 \text{ }\mu\text{m}$  as a separator, using a metal lithium foil having a thickness of  $500 \text{ }\mu\text{m}$  as a negative electrode, using a nickel foil of  $20 \text{ }\mu\text{m}$  as a negative electrode current collector, and using  $1\text{M LiPF}_6/\text{EC}+\text{DEC}$  (1:1) as an electrolyte.

With respect to one cell among them, charging was carried out to  $4.3 \text{ V}$  by a load current of  $75 \text{ mA per g}$  of the positive electrode active material at  $25^\circ\text{C}$ , and discharging was carried out to  $2.5 \text{ V}$  at a load current of  $75 \text{ mA per g}$  of the positive electrode active material,

whereby the initial discharge capacity was obtained.

Further, with respect to this cell, the charge/discharge cycle test was continuously carried out 30 times. As a result, the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 96.3%.

Further, with respect to the other cell, charging was carried out to 4.3 V at a constant current of 0.2 mA per 1 cm<sup>2</sup> of the positive electrode area and disassembled in the argon glove box, whereupon the positive electrode sheet after charging was taken out. The positive electrode sheet was washed and then punched out in a size of 3 mm, and it was sealed together with EC in an aluminum capsule. The temperature was raised at a rate of 5°C/min by a scanning differential calorimeter, whereby the heat generation initiation temperature was measured. As a result, the heat generation initiation temperature was 165°C.

#### EXAMPLE 2

A cobalt oxyhydroxide powder having a weight average particle size of 8 μm and a specific surface area of 50 m<sup>2</sup>/g, and a lithium carbonate powder having a weight average particle size of 15 μm and a specific surface area of 1.2 m<sup>2</sup>/g, were mixed. The mixing ratio was such that the composition would be LiCoO<sub>2</sub> after firing. These two types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen

concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing, the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}\alpha$  ray, the half-width of the diffraction peak for (110) face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.095^\circ$ . The packing press density of this lithium cobalt composite oxide powder was determined in the same manner as in Example 1, and found to be  $3.01 \text{ g/cm}^3$ .

Two simple closed cells were assembled in an argon glove box in the same manner as in Example 1 except that the above  $\text{LiCoO}_2$  powder thus obtained was used instead. With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at  $25^\circ\text{C}$  was 148 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 97.0%.

Further, in the same manner as in Example 1, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was  $169^\circ\text{C}$ .

### EXAMPLE 3

A cobalt oxyhydroxide powder having a weight average

particle size of 12  $\mu\text{m}$  and a specific surface area of 66  $\text{m}^2/\text{g}$ , and a lithium carbonate powder having a weight average particle size of 28  $\mu\text{m}$  and a specific surface area of 0.43  $\text{m}^2/\text{g}$ , were mixed. The mixing ratio was such  
5 that the composition would be  $\text{LiCoO}_2$  after firing. These two types of powders were dry-blended and then fired at 890°C for 18 hours in an atmosphere having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

10 With respect to the powder after the firing, the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using  $\text{CuK}_\alpha$  ray, the half-width of the diffraction peak for (110)  
15 face in the vicinity of  $2\theta = 66.5 \pm 1^\circ$ , was  $0.083^\circ$ . The packing press density of this lithium cobalt composite oxide powder was determined in the same manner as in Example 1, and found to be  $3.12 \text{ g/cm}^3$ .

Two simple closed cells were assembled in the same  
20 manner as in Example 1 except that the above  $\text{LiCoO}_2$  powder thus obtained was used instead. With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 1, whereby the initial  
25 discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 95.3%.

Further, in the same manner as in Example 1, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was 173°C.

#### COMPARATIVE EXAMPLE 1

LiCoO<sub>2</sub> was synthesized in the same manner as in Example 3 except that a cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) powder having a weight average particle size of 8 μm and a specific surface area of 0.66 m<sup>2</sup>/g was used instead.

With respect to the powder after the firing, the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face was 0.133°. The packing press density of this lithium cobalt composite oxide powder was determined in the same manner as in Example 1, and found to be 2.75 g/cm<sup>3</sup>.

Two simple closed cells were assembled in an argon grove box in the same manner as in Example 1 except that the LiCoO<sub>2</sub> powder thus obtained was used instead. With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 96.4%.

Further, in the same manner as in Example 1, with

respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was 155°C.

5 COMPARATIVE EXAMPLE 2

LiCoO<sub>2</sub> was synthesized in the same manner as in the above Example 3 except that a cobalt oxyhydroxide powder having a weight average particle size of 30 μm and a specific surface area of 7 m<sup>2</sup>/g was used instead. With  
10 respect to the powder after the firing, the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) was 0.118°. The packing press density of this lithium cobalt composite oxide powder was determined in the same  
15 manner as in Example 1, and found to be 3.15 g/cm<sup>3</sup>.

Two simple closed cells were assembled in an argon grove box in the same manner as in Example 1 except that the LiCoO<sub>2</sub> powder thus obtained was used instead. With respect to one of them, the initial electric capacity of  
20 the cell and the capacity after 30 cycles were obtained in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 137 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 92.3%.

25 Further, in the same manner as in Example 1, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte



was determined, whereby the heat generation initiation temperature was 158°C.

### COMPARATIVE EXAMPLE 3

LiCoO<sub>2</sub> was synthesized in the same manner as in the  
5 above Example 2 except that the firing was changed to the  
firing at 780°C for 12 hours. With respect to the powder  
after the firing, the measurement was carried out in the  
same manner as in Example 1, whereby the half-width of  
the diffraction peak for (110) face was 0.138°. The  
10 packing press density of this lithium cobalt composite  
oxide powder was determined in the same manner as in  
Example 1, and found to be 2.98 g/cm<sup>3</sup>.

Two simple closed cells were assembled in an argon  
grove box in the same manner as in Example 1 except that  
15 the LiCoO<sub>2</sub> powder thus obtained was used instead. With  
respect to one of them, the initial electric capacity of  
the cell and the capacity after 30 cycles were obtained  
in the same manner as in Example 1, whereby the initial  
discharge capacity at from 2.5 to 4.3 V at 25°C was 147  
20 mAh/g, and the capacity retention after 30  
charge/discharge cycles, was 96.5%.

Further, in the same manner as in Example 1, with  
respect to the other cell, the reactivity of the charged  
positive electrode active material with the electrolyte  
25 was determined, whereby the heat generation initiation  
temperature was 156°C.

**[Effects of the Invention]**

By employing as a positive electrode active material, the hexagonal lithium cobalt composite oxide for a lithium secondary cell obtained by the production  
5 method of the present invention, a non-aqueous electrolyte secondary cell which is useful within a wide voltage range, and excellent in the electric capacity and charge/discharge cycle durability, and has excellent low temperature operation efficiency and safety, will be  
10 provided.

【TYPE OF DOCUMENT】

ABSTRACT

【SUMMARY】

【OBJECT】

A composite oxide for a non-aqueous electrolyte  
5 secondary cell which is useful in a wide voltage range  
and excellent in the charge/discharge cycle durability,  
and has a high electric capacity and excellent low  
temperature operation efficiency.

【MEANS OF SOLVING PROBLEMS】

10 The composite oxide is obtained by dry blending a  
cobalt oxyhydroxide powder having an average particle  
size of from 1 to 20  $\mu\text{m}$  and a specific surface area of  
from 2 to 200  $\text{m}^2/\text{g}$ , a lithium carbonate powder having an  
average particle size of from 1 to 50  $\mu\text{m}$  and a specific  
15 surface area of from 0.1 to 10  $\text{m}^2/\text{g}$ , and firing the  
mixture at a temperature of from 850 to 950°C in an  
oxygen-containing atmosphere for from 4 to 30 hours.

【SELECTED FIGURE】

No Selected Figure